

A Nonempirical Heisenberg Hamiltonian for the Study of Conjugated Hydrocarbons. Ground-State Conformational Studies

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Abstract: A magnetic effective valence bond Hamiltonian of the Heisenberg type is extracted from ab initio (extended basis sets and CI's) calculations on ethylene lowest states. The σ potential R_{ij} and the effective exchange integral g_{ij} between adjacent atoms are functions of the r_{ij} distance and torsional angle θ_{ij} around the ij bond. This simple model allows a direct and efficient geometry optimization of any neutral state (in the sense of valence bond theory) of conjugated hydrocarbons. The ground-state conformations agree very well with experiment and refined ab initio calculations. Rotational barriers (including geometry relaxation) are easily obtained. The method gives the energy difference between unstrained conjugated isomers and Jahn-Teller distortions in degenerate problems. The model applies successfully to open-shell systems and might be of great interest for the study of polyacetylene and soliton problems. Asymptotic values of rotational barriers are predicted.

I. Introduction

The Heisenberg magnetic Hamiltonians,¹ which have been essentially developed in solid-state physics for Mott insulators, sometimes have been applied to the π systems of conjugated molecules (see, for instance, footnotes 2 and 3). Two preceding papers^{4,5} (hereafter called I and II) have applied the "Quasi-degenerate perturbation theory"⁶⁻¹¹ to the valence bond problem, defining the neutral configurations (with one electron per atom) as the model space which spans a magnetic effective Hamiltonian. The procedure, which is a generalization of the Anderson's approach for solid-state physics,¹² results in a very simple Hamiltonian dominated by effective exchange interactions between adjacent atoms. A similar Hamiltonian has been derived independently by a completely different approach by Kuwajima.¹³ When the quasi-degenerate perturbation theory diverges, other iterative variational procedures,¹⁴ derived from the Bloch equation, may be used to build the effective magnetic operators, leading to the same structure of the effective Hamiltonian.¹⁵

Of course, this Heisenberg-type Hamiltonian, which reduces the information on the wave functions to neutral situations, can only deliver a definite number of eigenvalues of the full problem, those which concern the "neutral" states in the sense of valence bond theory. The ionic situations are not explicitly introduced; they simply result in effective couplings between the neutral determinants, and the eigenstates, which are essentially ionic, such as the lowest allowed ¹B_u excited singlet state of linear polyenes, do not appear in the calculated spectrum. But the effective valence bond approaches, which require the diagonalization of much smaller matrices than the full CI, give simultaneously several states with an equal accuracy and make possible rational studies of excited states which are difficult to achieve from the MO-CI canonical treatment.

Our previous work (and the analysis of the resulting projected wave functions¹⁶) dealt with an effective Hamiltonian which was extracted from a reference Hubbard¹⁷ or PPP¹⁸ π Hamiltonian, and could at best reproduce the full CI of this reference Hamiltonian. The σ core was ignored, and the use of the π electronic energy for conformational studies required either empirical relationship (such as bond-length- π index relationships¹⁹) or the introduction of an empirical σ potential (for a powerful application of this approach, see Lasaga et al.²⁰). However, the σ - π interaction is much more subtle than a simple addition; for nonplanar conformations, hyperconjugation occurs, which plays an important role in rotational barriers, and it has been shown that the spin polarization of the σ core is responsible for the singlet < triplet

energy ordering of twisted ethylene.²¹

The present paper proposes a very simple nonempirical Heisenberg-type Hamiltonian which has been extracted from ab initio extended basis set CI calculations on ethylene lowest singlet and triplet states. The two parameters of the model incorporate the σ and π energy dependence to the bond length and bond twisting; the model is applied to ground-state conformational studies and proves to give very reliable results at a low expense. Possible generalizations and improvements of the model are discussed in the last section. The following paper is devoted to excited-state studies.

II. Nonempirical Heisenberg Model for Conjugated Systems

(A) Determination of a Two-Body Magnetic Operator. The structure of the magnetic effective valence bond Hamiltonian has been given previously^{4,5} including two-, three-, four-, and six-body operators. The two-body operators are by far dominant; the four-

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- (13) S. Kuwajima, *J. Chem. Phys.*, **77**, 1930 (1982).
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- (19) Such a relation has been proposed in ref 16 for Heisenberg Hamiltonians; it is analogous to the bond order/bond lengths relationships in MO theories (for a review see, for instance, L. Salem, "The Molecular Orbital Theory of Conjugated Systems", W. A. Benjamin, New York, 1966).
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and six-body terms essentially play a role on four- and six-membered rings, respectively, and are unimportant on noncyclic conjugated hydrocarbons. The two-body Heisenberg operator keeps the form

$$H^{\text{eff}} = \sum_{ij \text{ bonded}} g_{ij} [a_i^+ a_j^+ a_j a_i + a_j^+ a_i^+ a_i a_j - a_i^+ a_j^+ a_j a_i - a_i^+ a_j^+ a_i^+ a_j] + R$$

$$= \sum_{ij \text{ bonded}} g_{ij} [|\bar{i}\bar{j}\rangle \langle \bar{i}\bar{j}| - |\bar{i}\bar{j}\rangle \langle i\bar{j}| + |\bar{i}\bar{j}\rangle \langle i\bar{j}| - |\bar{i}\bar{j}\rangle \langle \bar{i}\bar{j}|] + R \quad (1)$$

where R is a constant dependent on the molecular conformation. The diagonal operators stabilizes the determinants ϕ_1 which possess a spin alternation on the ij bond, while the off-diagonal ones couple a determinant ϕ_1 with the $i\bar{j}$ distribution on the ij bond with a determinant ϕ_j which only differs from ϕ_1 by a spin permutation (i.e., a $i\bar{j}$ distribution) on the ij bond. For a two-center problem, i.e., for ethylene, the ($S_z = 0$) problem reduces to a 2×2 matrix

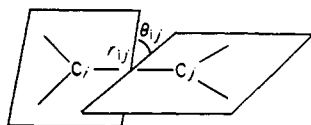
$$\begin{bmatrix} |1 & \bar{2}| & |\bar{1} & 2| \\ R - g_{12} & g_{12} & & \\ & & R - g_{12} & \\ & & & \end{bmatrix} \rightarrow \begin{cases} E(T^1) = R \\ E(S^1) = R - 2g_{12} \end{cases}$$

the solutions of which are the singlet state $[|\bar{1}\bar{2} - \bar{1}2]/\sqrt{2}$, the energy of which (1E) is $R - 2g_{12}$, and the triplet state $[|\bar{1}\bar{2} + \bar{1}2]/\sqrt{2}$, the energy of which (3E) is R . Then the basic quantities are immediately obtained

$$R = {}^3E \quad (2)$$

$$g = ({}^3E - {}^1E)/2 \quad (3)$$

as has been done recently by Poshusta and Klein²² for the H_2 molecule and H_n chains. Then if one knows the potential surfaces of the lowest singlet and triplet states, the parameters R and g may be obtained as functions of the geometric conformation. They may be obtained as functions of the interatomic distance r_{ij} and of the twist angle θ_{ij} between the two CH_2 groups (i.e., of two $2p_z$



atomic orbitals). One might also study their dependence on the pyramidalization angle ϕ_i of one of the carbon atoms going from the planar (sp^2) conformation to a tetrahedral (sp^3 type) conformation, but the present work has disregarded this degree of freedom, which essentially plays a role in ionic excited states²³⁻²⁶ and in the so-called "sudden polarization" problem.²⁷⁻³⁰

The potential energy surface of ethylene ground and lowest triplet states have been obtained through an ab initio calculation as a function of r and θ . The basis set was of standard double $\zeta + d$ quality, and the CI performed according to the perturbative CIPSI scheme^{31,32} from a variational multireference zeroth-order wave function involved up to 10^5 configurations. The $R(r, \theta)$ and

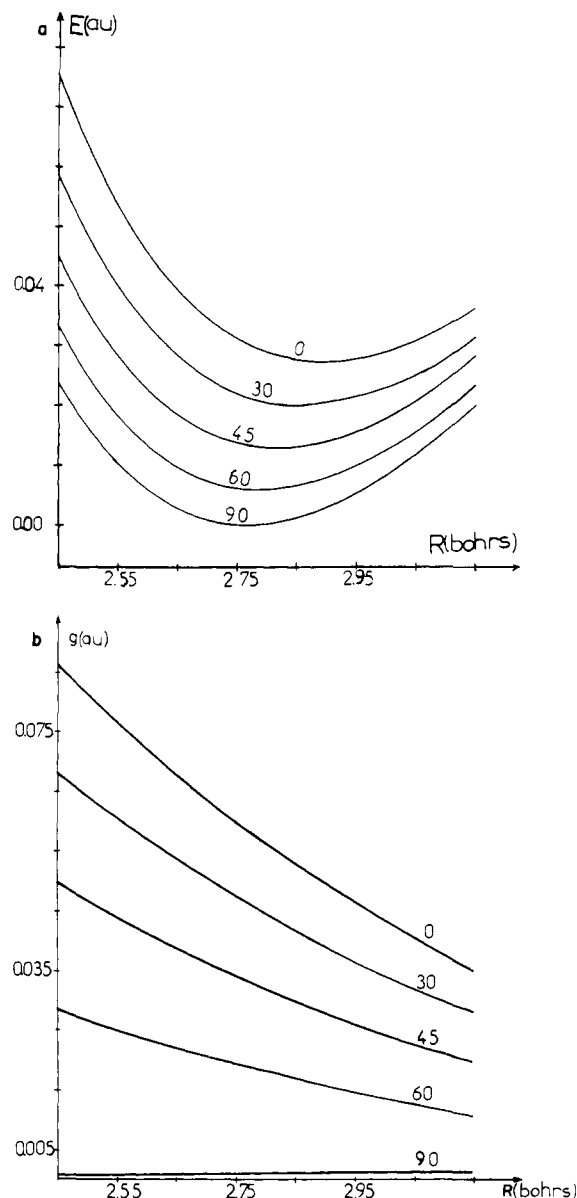


Figure 1. (a) Dependence of $R(r)$ on the interatomic distance r for different values of the torsional angle θ . This represents the 3B_u excited-state surface of ethylene. (b) Dependence of the effective spin-coupling operator $g(r)$ on the interatomic distance for different values of the torsional angle θ . (The singlet ground-state 1A_g surface of ethylene is given by $R(r) - 2g(r)$.)

$g(r, \theta)$ functions are given in Figure 1a,b and have been fitted in a polynomial expansion as a function of r for each value of θ . The ground- and excited-state equilibrium characteristics given hereafter may be compared with the experimental characteristics or good CI ab initio calculations:³³

1A_1 ground state:

$$R_{cc} = 1.344 \text{ \AA} \quad (\text{exptl } 1.339 \text{ \AA}, {}^{34} \text{ MO-CI } 1.336 \text{ \AA}^{33})$$

$$k_{cc} = 9.29 \text{ mdyn/\AA} \quad (\text{exptl } 9.395 \text{ mdyn/\AA}, {}^{35} \text{ MO-CI } 9.56 \text{ mdyn/\AA}^{33})$$

$$\text{torsional barrier} = 61 \text{ kcal/mol}$$

Twisted triplet excited state:

$$R_{cc} = 1.463 \text{ \AA} \quad (\text{MO-CI } 1.462\text{--}1.459 \text{ \AA}, {}^{33} 1.46 \text{ \AA}, {}^{24} 1.48 \text{ \AA}^{36})$$

$$k_{cc} = 5.78 \text{ mdyn/\AA} \quad (\text{MO-CI } 5.77, 5.51 \text{ mdyn/\AA}^{33})$$

adiabatic $S_0 \rightarrow T$, transition energy =

$$62.5 \text{ kcal/mol} \quad (62 \text{ kcal/mol}^{36}, 66.6 \text{ kcal/mol}^{33})$$

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(30) For reviews, see L. Salem, *Acc. Chem. Res.*, **12**, 87 (1979); J. P. Malrieu, *Theor. Chim. Acta*, **9**, 251 (1981).

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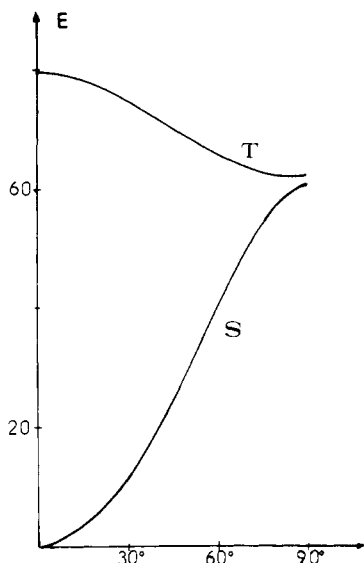


Figure 2. Energy variation (in kcal/mol) of the lowest singlet and triplet state of ethylene under double-bond torsion. The C-C bond length is optimized for each value of θ .

The θ dependence of the singlet and triplet optimized energies is plotted in Figure 2. The variation of the optimized internuclear distance r_{ij} under the torsion of the bond is plotted in Figure 3, showing a nonlinear progression.

Once these two basic parameters have been extracted from ethylene, one may solve the effective Hamiltonian of eq 1 for any conjugated molecule. The Hamiltonian, of Heisenberg type, is restricted to two-body terms, and one should consider only the g_{ij} interactions between chemically bonded atoms (tight-binding approximation) at the present stage since the g_{ij} effective spin interaction between atoms in relative position 1-3 cannot be extracted from a distorted ethylene molecule. (Anyway it appears from Figure 1b that it would be very small for distances around 2.4 Å.)

One must include the R constant which is the energy of the neutral eigenstate of highest multiplicity (quintuplet for butadiene, septuplet for hexatriene, $(n+1)$ -uplet for n carbon atoms), i.e., of the state where all spins would be parallel and which represents the zero of energy for the molecule. This energy is actually purely of σ type since no delocalization nor correlation is possible in the π subset and may be considered as bond additive, as usually done with great success for saturated molecules.³⁷ Then

$$R = \sum_{ij \text{ bonds}} R_{ij} \quad (4)$$

The research of the solutions of H^{eff} (eq 1) consists of the diagonalization of H^{eff} in the basis of the $C_n^{n/2}$ ($S_z = 0$ or $S_z = 1/2$) neutral determinants which represent all the possible spin distributions of $n/2$ electrons of α spin and $n/2$ electrons of β spins on n carbon atoms, each bearing one electron only. This number increases rapidly when n increases, but this diagonalization remains infinitely more rapid than the full CI diagonalization (even restricted to the π electrons in a minimal basis set). It may be significantly reduced by a proper partition into blocks of different $\langle S^2 \rangle$ values.

The present Hamiltonian takes into account the hyperconjugation (σ - π mixing) in twisted conformations which can hardly be included in the methods which rest on the σ - π separation and the additivity of σ and π energies. As one may notice from Figure

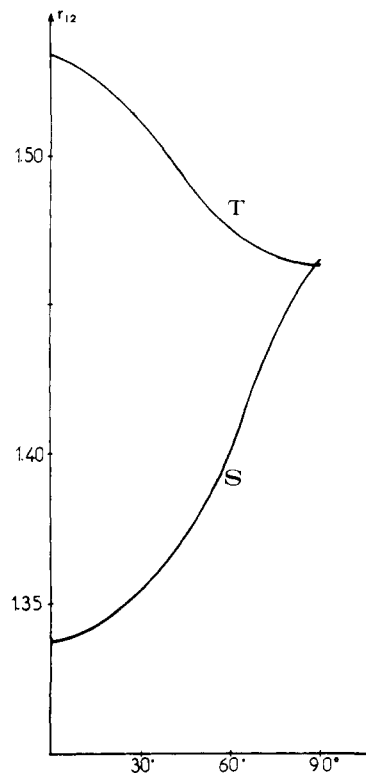


Figure 3. Optimized interatomic C-C distances for 1A_g and 3B_u states of ethylene (in Å) as functions of the torsional angle.

1b, the g parameter remains positive (i.e., antiferromagnetic) for $\theta = 90^\circ$ where the conjugation disappears, and where simple schemes could lead to a zero or slightly negative value. This is due to the inclusion of the double-spin polarization effect of the σ core which is responsible for the singlet < triplet energy ordering.²¹ The three-body operators which should be extracted from analogous studies on the allyl system have not been included but it has been shown before that they are smaller by a factor of 10 than the two-body terms and they should not affect severely the calculated conformations.

The evident main defect of the model concerns the long-distance repulsive interactions in the σ system (and particularly the repulsion between the hydrogen atoms on the terminal carbons 1 and 4 of butadiene, which are responsible for the energy difference between its cis and trans conformers), 2.3 kcal/mol in the rigid rotator model. Such a repulsion might be introduced a posteriori through a small exponential term as done in most molecular potentials calculations.

(B) **Geometry Optimization.** When applied to a polyatomic molecule in a definite conformation, the effective Hamiltonian (eq 1) gives a set of vectors of various spin and space symmetries. It has been proved elsewhere¹⁶ that if $R = 0$, the π energy E_1 of a given eigenstate ψ_1

$$H^{\text{eff}}(\psi_1) = E_1(\psi_1)$$

may be obtained from ψ_1 eigenstate spin characteristics as

$$E_1 = \sum_{ij \text{ bonded}} -2g_{ij} \mathcal{P}_{ij}^{S,1} \quad (5)$$

where $\mathcal{P}_{ij}^{S,1}$ is the probability of finding a π singlet arrangement between the bonded atoms i and j

$$\mathcal{P}_{ij}^{S,1} = \frac{1}{2} \langle \psi_1 | \vec{i} \cdot \vec{j} - \vec{i} \vec{j} | \psi_1 \rangle \quad (6)$$

Adding the R constant (eq 4), the total energy may be expressed as

$$E_1 = \sum_{ij \text{ bonds}} [R_{ij} - 2g_{ij} \mathcal{P}_{ij}^{S,1}] \quad (7)$$

Then the geometry optimization may proceed from bond to bond

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(37) For a review, see J. P. Daudey, J. P. Malrieu, and O. Rojas, "Localization and Delocalization in Quantum Chemistry, O. Chalvet et al., Eds., Reidel, Dordrecht, 1975, p 155.

$$\frac{\partial E_1}{\partial r_{ij}} = \frac{\partial R_{ij}}{\partial r_{ij}} - 2\mathcal{P}_{ij}^{S,1} \frac{\partial g_{ij}}{\partial r_{ij}} - 2g_{ij} \frac{\partial \mathcal{P}_{ij}^{S,1}}{\partial r_{ij}} + \sum_{kl} 2g_{kl} \frac{\partial \mathcal{P}_{kl}^{S,1}}{\partial r_{ij}} \quad (8)$$

(and an analogous equation for the twist angle around the ij bond).

Since the wave function is almost stationary near the energy minimum, one may neglect the derivative of the wave function characteristic and use

$$\frac{\partial E_1}{\partial r_{ij}} \approx \frac{\partial R_{ij}}{\partial r_{ij}} - 2\mathcal{P}_{ij}^{S,1} \frac{\partial g_{ij}}{\partial r_{ij}} \quad (9)$$

The R_{ij} and g_{ij} functions being fitted by polynomials (given in the Appendix I), the condition

$$\partial E_1 / \partial r_{ij} = 0 \quad (10)$$

is immediately satisfied and delivers an "optimal" value of r_{ij} . The process is simultaneously performed on all bonds. Starting from a guess geometry G_0 , one diagonalizes H^{eff} , obtains the singlet probabilities on the various bonds for the desired wave function ψ_1 , and applies eq 9 and 10 to reach a new geometry G_1 ; the process is repeated to self-consistency (and energy minimization). A few iterations are sufficient to reach the minimum from standard geometries, even for excited states (cf. Appendix II).

(C) π Delocalization and Resonance Energies. In such a model, the π delocalization energy might be defined by reference to the multiplet of highest multiplicity (all spin parallels) which does not allow any conjugation; such a multiplet would exhibit a fully twisted conformation with all successive $2p_z$ orbitals in perpendicular orientations.



Its conformation and energy are immediately given by

$$E_{S, \max} = \sum_{ij \text{ bonds}} R_{ij} = n_b R_{\min}$$

where n_b is the number of conjugated bonds and R_{\min} the minimum energy of the ethylenic triplet (in its perpendicular conformation).

The π delocalization energy of a given state I may then be defined as

$$\Delta E_1 = n_b R_{\min} - E_1$$

E_1 being the eigenvalue of the effective Hamiltonians. The delocalization energy per electron will be

$$\epsilon_1 = \Delta E_1 / n$$

n being the number of conjugated carbon atoms (and π electrons); the resonance energy might be defined as the difference between the π delocalization energy and the energy of a fully localized Kekulean structure, involving \hat{n} double bonds without any conjugation between them. If E_1 is the singlet ground-state equilibrium energy of ethylene, the resonance energy will be

$$\Delta E_{R,1} = \hat{n}E^1 + (n_b - \hat{n})R_{\min} - E_1 = \Delta E_1 - \hat{n}(E^1 - R_{\min}) = \Delta E_1 - \hat{n}(\Delta E_{0,2})$$

where $\Delta E_{0,2}$ is the π delocalization energy of the ethylene molecule (0.100 au i.e., the $S_0 \rightarrow T_1$ adiabatic transition energy of this molecule, almost equal to the rotational barrier of ethylene).

III. Results

(A) **Bond Alternation in Linear Polyenes and Annulenes.** As well known and as expected from a previous analysis of the magnetic wave function,^{2,16} the optimized geometries of linear polyenes (Figure 4) exhibit a strong bond alternation. The shortest bonds are the external double bonds (1.353 Å), while the internal double bonds are slightly larger (1.365 Å in decapentene, 5–6 bond); the single bonds lie between 1.445 and 1.438 Å (the latter value concerning the central bond of decapentene). The results exhibit a very slight tendency for a decrease of bond alternation in the center of long polyenes.

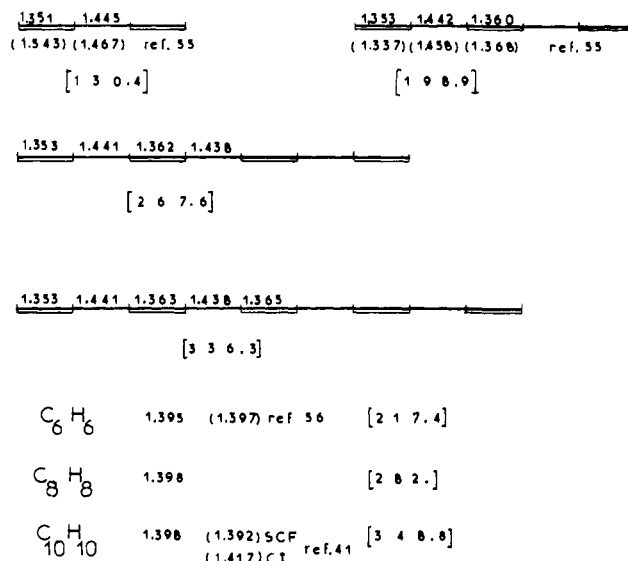


Figure 4. Optimized bond lengths (in Å) for even linear polyenes and annulenes. The numbers between hooks are the π delocalization energies (in kcal/mol). The bond-length values in parentheses come from either experiment or recent ab initio calculations.

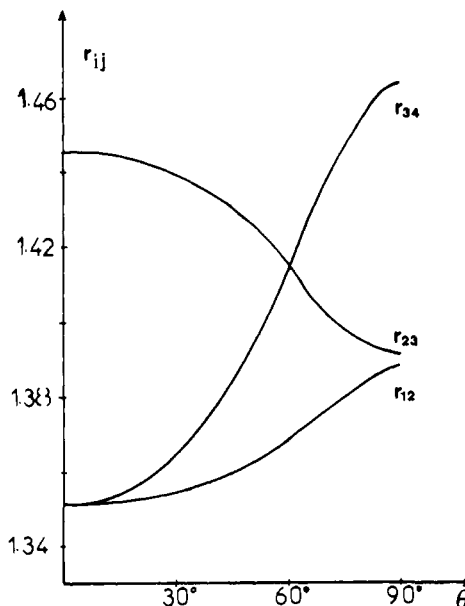


Figure 5. Optimized interatomic C-C distances for the ground state of butadiene (in Å) as functions of the torsional angle around the C_3 - C_4 double bond.

These results are in perfect agreement with experiment, as well as the internal rotation barrier around single bonds (5.4 kcal/mol, in butadiene, 5 to 7 from experiment),^{38,39} which confirms that our method correctly takes into account the interplay between conjugation and hyperconjugation responsible for this barrier.⁴⁰

The barrier to rotation of the double bond of butadiene (51.2 kcal/mol) is significantly lower than that of ethylene. The evolution of the rotational barriers amplitude in the series of linear polyenes will be discussed later on. The bond-length changes are given in Figure 5, and may be compared with the bond-length changes of ethylene (Figure 3). One may notice that there is no difficulty in calculating a ground-state rotational barrier around a double bond while the MO approaches face a methodological

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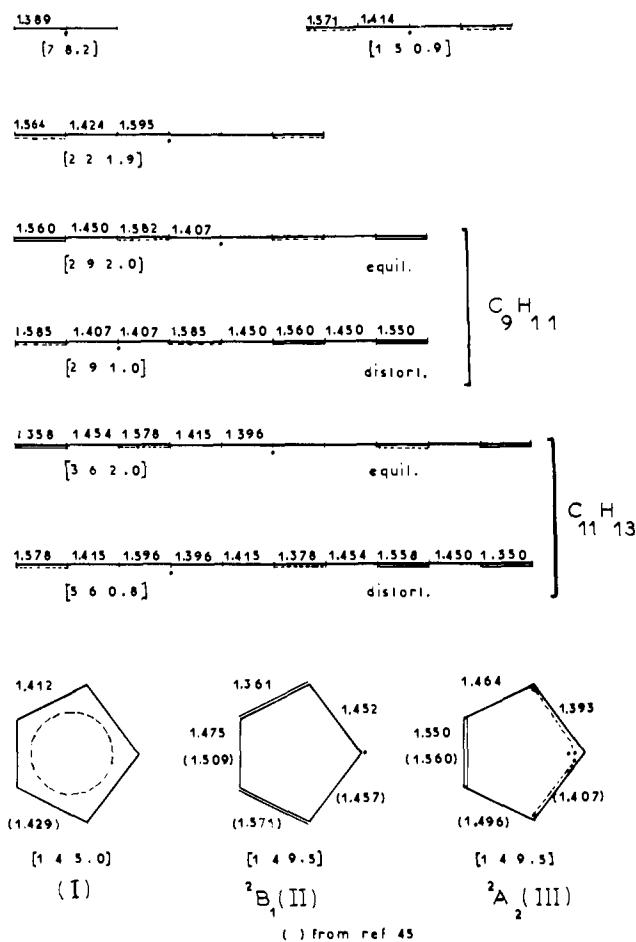


Figure 6. Optimized bond lengths (in Å) for odd linear polyenes and annulenes. Same comments as for Figure 4.

dilemma: the planar and weakly twisted conformations call for a closed-shell description of the ground state, while in the perpendicular conformation the ground state becomes biradicalar and requires an open-shell treatment; there is no easy way to go from one description to the other one without introducing some discontinuity in the potential curve, except through very large CI's. An alternative approach would consist of a multiconfigurational treatment. Most of the theoretical estimates of ground-state double-bond rotational barriers have to be deduced from the triplet excited-state energy minimization.

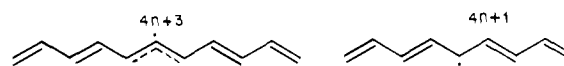
For small n annulenes the method faces a methodological problem since some specific cyclic n -body operators of the effective Hamiltonian have been shown to play an important role.⁴⁵ These operator should be extracted from ab initio calculations on cyclobutadiene and benzene. Since the four-body terms have been shown to be very important in four-membered rings (their amplitude reaching 0.8 eV), the present model will not try to treat such molecules. The sixth-body operators in benzene have a much lesser amplitude (~ 0.3 eV), and the two-body Heisenberg Hamiltonian is sufficient to predict a regular cyclic geometry for benzene ($r = 1.395$ Å) in perfect agreement with experiment. The same optimization has been performed for planar cyclooctatetraene and cyclodecapentene (which actually are not planar because of σ constraints) in order to study the possible tendency for bond alternation to appear, and the optimal geometry was found to exhibit equal bond lengths (1.398 Å in [8]- and [10]annulene in agreement with recent ab initio CI calculations⁴¹ (1.392 Å at the Hartree-Fock level, 1.417 Å at the second-order Møller-Plesset level of the CI treatment).

(B) Odd Polyenes and Annulenes (Figure 6). The allyl optimal geometry is symmetrical ($r = 1.389$ Å) in agreement with ab initio

CI results⁴² (despite the tendency to break the symmetry at the Hartree-Fock level, which gave rise to a series of discussion seven years ago⁴³). The bond length is intermediate between single and double bonds.

Pentadienyl and larger odd polyenes all keep the central symmetry. One may notice from Figure 6 an increasing tendency to restore bond alternation on the external bonds. The most external bond length C_1-C_2 goes from 1.371 Å for $n = 5$ to 1.364 Å for $n = 7$, 1.360 Å for $n = 9$, and 1.358 Å for $n = 11$, while the next bond C_2-C_3 goes from 1.414 Å for $n = 5$ to 1.424 Å for $n = 7$, 1.430 Å for $n = 9$, and 1.434 Å for $n = 11$. The central bonds are closer to the intermediate bond length (1.39 or 1.40 Å). From the bond lengths of the highest odd polyene reported here, it is clear that the odd linear chains may be depicted as a free-radical deformation centered in the middle of the molecule, its deformation being limited to a rather small number of bonds. Further comments will be devoted in the conclusion to this question which is part of the soliton problem.⁴⁴

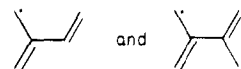
One may notice (cf. Figure 6) that for $4n + 3$ radicals the central bond lengths are somewhat shorter than for $4n + 1$ radicals although the asymptotic value should be the same. This difference may be understood as an end effect, the central bonds keeping a double (respectively single) bond character in $4n + 3$ (respectively $4n + 1$) molecules:



Among odd annulenes, cyclopentadienyl has been studied for comparison with the ab initio analysis of its Jahn-Teller deformation.⁴⁵ The optimal cyclic geometry (I) ($r_e = 1.412$ Å) is a saddle point lying 4.5 kcal/mol above two degenerate minima of C_{2v} symmetry, one having a (butadiene + methyl) structure (labeled II in Figure 6) and a 2B_1 symmetry, while the other (III) looks like a (ethylene + allyl) complex with a 2A_2 symmetry. The amplitude of this Jahn-Teller distortion compares favorably with the ab initio estimate (7 kcal/mol), and our calculated bond lengths for structures I, II, and III compare very well with the ab initio results of Davidson et al.,⁴⁵ whose bond lengths are certainly overestimated by the use of a minimal basis set.

(C) Branched Molecules (Figure 7). The simplest branched molecule is trimethylenemethane, the ground state of which is a triplet with equal bond lengths (1.405 Å) in good agreement with the ab initio CI result of Davidson et al.⁴⁵ (1.429 Å). These authors have discussed the properties of the lowest singlet state in great details and our results agree with theirs. The most stable singlet conformation (II) is twisted around one bond and lies 17 kcal/mol above the triplet (cf. 14 kcal/mol in the ab initio calculation of ref 46) while the planar singlet geometries are distorted by a Jahn-Teller effect in either a 1B_2 (III) or 1A_1 (IV) which are degenerate, 34 kcal/mol above the triplet ground state.

Two larger branched molecules may be viewed as a butadiene substituted by one (or two) CH_2 group on the central bond, such as



The optimized geometry does not retain this qualitative description and tends to restore a D_{2h} (or nearly D_{2h}) symmetry through an equalization of the possibly resonating $C-C=C$ systems. The resulting structures agree better with the qualitative pictures allyl + ethylene (i) or allyl + allyl (ii) than with the previously sug-

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(43) J. M. McKelvey and W. J. Hehre, *Chem. Phys. Lett.*, **41**, 476 (1976); J. Paldus and A. Veillard, *ibid.*, **50**, 6 (1977).

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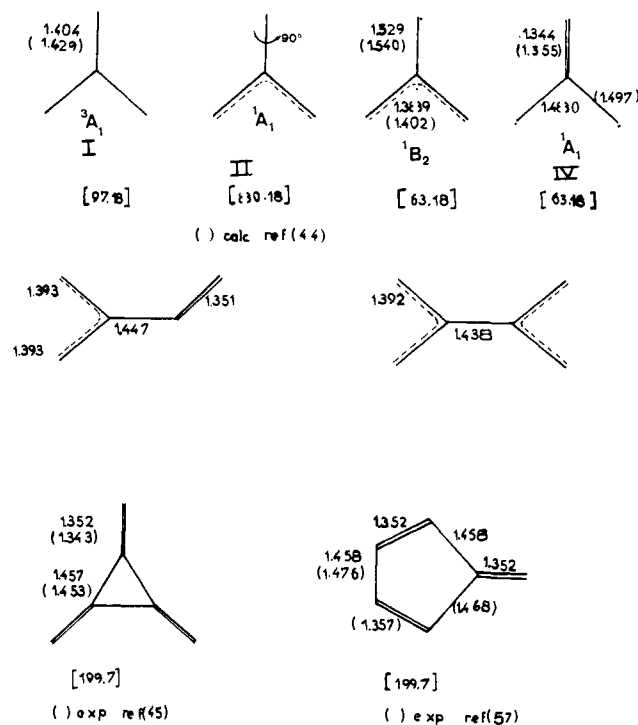
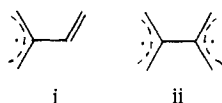


Figure 7. Optimized bond lengths (in Å) for branched conjugated hydrocarbons. The singlet excited-state geometries are also reported for trimethylenemethane. Same comments as for Figure 4.



gested description of a butadiene molecule substituted by methylene groups.

Trimethylenecyclopropane (a conjugated isomer of benzene molecule) agrees very well with the results of electron diffraction⁴⁷ (within 0.01 Å). The agreement is almost as excellent (0.02 Å) for fulvene, another nonalternant C_6H_6 conjugated molecule.

(D) Polycyclic Compounds and Branched Aromatic Compounds (Figure 8). The method applies to nonaromatic and aromatic compounds, alternant and nonalternant molecules, as well as polycyclic compounds. (As an example of a nonaromatic nonalternant hydrocarbon, fulvene has already been mentioned.)

Two $C_{10}H_8$ bicyclic isomers have been studied, namely, naphthalene (aromatic alternant) and azulene (nonaromatic nonalternant). The naphthalene calculated geometry agrees with the experimental one within 0.01 Å (Figure 8). The stable azulene geometry (conformation I) appears to be C_s (broken symmetry with bond alternation, the largest deviation being again 0.02 Å from ab initio MO CI calculation⁴¹).

The C_{2v} symmetry solution (II) is nearly degenerate (0.035 eV above I); in this solution all bond lengths are nearly equal (≈ 1.39 , 1.40 Å, i.e., almost aromatic or annulenic), except for the bond belonging to both the seven- and five-membered rings, which remains very weak and long. One may notice that the C_2 symmetry conformation (II) represents a saddle point between the two equivalent broken symmetry minima I and I', with

$$r_{ij}^{(II)} = (r_{ij}^{(I)} + r_{ij}^{(I')})/2$$

which would make the interconversion very easy, and the observed bond lengths^{48,49} may correspond to a time average. These results should be compared with the recent ab initio values given by Haddon⁴¹ who finds the C_s symmetry minimum lower than the C_2 one at the STO-3G-SCF level but which reverses this order by 2.6 kcal/mol at the STO-6-31G-SCF level. The CI performed

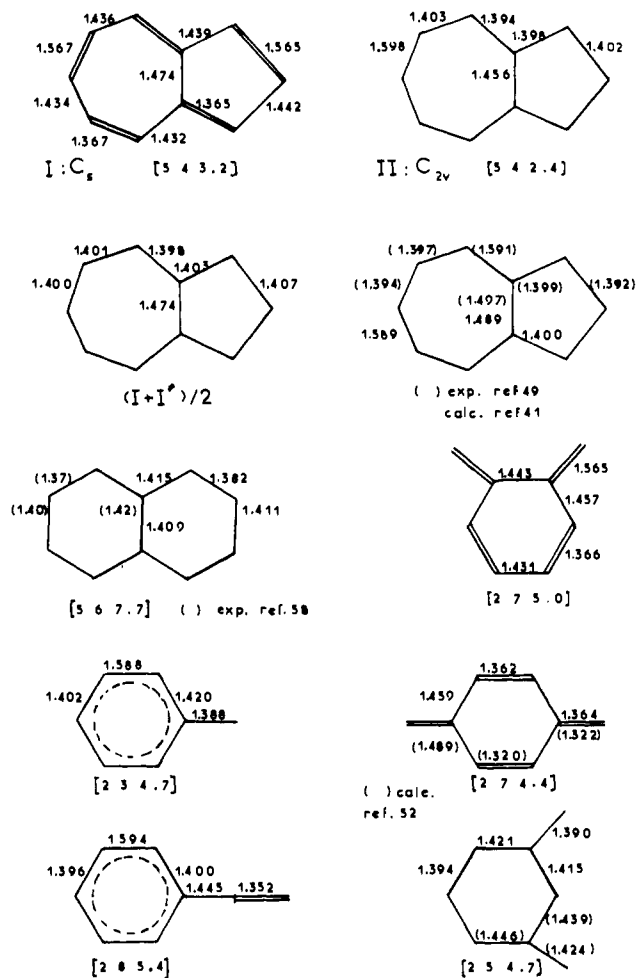


Figure 8. Optimized bond lengths in Å for polycyclic and aromatic branched molecules. Same comments as for Figure 4.

Table I. Ground-State π Delocalization Energy E_π in the Series of Linear C_nH_{n+2} Polyenes, and π Delocalization Energy per Electron (kcal/mol)

n	E_π	E_π/n
2	62.5	31.7
3	78.2	26.1
4	130.4	32.6
5	150.9	30.2
6	198.9	33.1
7	221.9	31.7
8	267.6	33.5
9	292.0	32.4
10	336.3	33.6
11	361.6	32.9

at the second-order MP level increases the stability of the C_{2v} minimum, but the geometry optimization was not achieved at the CI level, and the CI was necessarily very approximate. One may notice that the MP second-order result is not invariant under a unitary transformation of the MO's. These uncertainties are of the same order of magnitude as those of our model which does not take into account three-body operators and the angular distortion differential effect. Haddon tried to attribute the ground-state geometry from the dipole moment, but the difference between the dipole moments of the forms I and II is not large enough to give a reliable conclusion, and the problem seems to lie at the present borders of predictability of the theoretical tools. The same comments apply for [10]annulene.

Benzyl and styrene ground-state geometries have been studied too. In styrene the benzene ring keeps its aromatic character with

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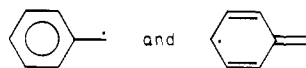
Table II. Rotational Barriers around Double and [Single] Bonds p , $p + 1$ of Even Polyenes (kcal/mol)^a

$n = p + q$	$p - q$					
	0	2	4	6	8	10
2	62.5					
4	[5.4]	52.2				
6	42.5	[6.0]	48.0			
8	[6.8]	38.5	[6.2]	45.7		
10	34.5	[7.0]	36.2	[6.2]	44.3	terminal
(12)	[6.8]	32	[6.6]	34	[5.8]	43 bonds
(14)	30	[6.9]	30	[6.7]	34	
(16)	[7.0]	28	[7.0]	30		
(18)	27	[6.9]	28			
(20)	26					

inner bonds

^a For $n > 10$ the energy of the planar singlet has been estimated from the extrapolation given in eq 11.

almost equal bond lengths (1.994 to 1.400 Å), and the external double bond is weakly conjugated with the benzenic ring through a rather long π bond ($l = 1.445$ Å). The benzene ring distortion is more pronounced in the benzyl free radical with a short extracyclic bond (1.388 Å), which may be interpreted as a resonance with a quinoid form



These quinoid forms dominate in *o*- and *p*-xylylenes which are strongly alternant, while *m*-xylylene diradical has aromatic (intermediate) bond lengths (between 1.39 and 1.42 Å). The later molecule appears to have a triplet ground state, as experimentally demonstrated.^{50,51}

The structure of *m*- and *p*-xylylenes should be compared with recent ab initio minimal basis set calculations,⁵² where the geometry optimization was performed at the SCF level. The difference is larger than for other compounds. The lowest vertical transition energy ${}^3B_2 \rightarrow {}^1A_1$ is 33 kcal/mol; the diabatic energy difference falls to 28 kcal/mol while it has been calculated to be 10 kcal/mol in the above-mentioned ab initio calculation using a Dunning split-valence basis set and an STO-3G three configuration SCF geometry optimization of the 1A_1 state. The equilibrium conformations are also compared in Figure 8.

(E) Energetic Features: Rotational Barriers, Resonance Energy per Electron, and Isomerization Energies. Although the π delocalization energy and the resonance energy are not observable, it may be useful to compare these quantities with their usual MO estimates. One may notice from Table I that the π delocalization energy per electron is almost constant in the series of even polyenes (slowly increasing to 34 kcal/mol) and starts from lower values for small odd polyenes (26.3 kcal/mol for allyl), increasing asymptotically for large odd n to the same value as for even n . The closeness of these quantities is remarkable in view of the difference in geometries. The fact that $E_\pi(2n)/2n$ and $E_\pi(2n + 1)/(2n + 1)$ tend toward the same asymptote is not surprising since the rotational barrier around a double bond tends to a constant

$$E_0(2n) - E_0^\perp(2n) = C$$

E_0^\perp being the energy of a twisted conformation of the even polyene, for instance, around its terminal double bond. The orthogonality of the $(2n - 1)$, (1) subsystems implies, neglecting hereafter the small exchange on the twisted bond

$$E_0^\perp(2n) = E_0(2n - 1) + R_{\min}$$

$$[E_\pi(2n) - E_\pi(2n - 1)]/2n \rightarrow 0 \text{ as } n^{-1} \text{ when } n \rightarrow \infty$$

(50) G. Kothe, K. H. Denkel, and W. Suemmermann, *Angew. Chem., Int. Ed. Engl.*, **9**, 906 (1970).

(51) B. B. Wright and M. J. Platz, *J. Am. Chem. Soc.*, **105**, 628 (1983).

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The n dependence of the rotational barrier of a linear polyene is studied in the next section.

We have reported in Table II the calculated rotational barriers of a series of linear polyenes. The rotational barriers, ΔR , for a twist around the $2p - 1$, $2p$ double bond are immediately estimated from

$$\Delta R_{2p-1,2p} = E_{(2p-1)} + E_{(2n-2p+1)} + R_{\min} - E_{(2n)}$$

These quantities are not rigid rotator energies; they include the bond-length relaxations in the perpendicular conformation.

Two main features appear from Table II: (i) the rotational barrier decreases when $2n$ increases, whatever the position of the twisted bond (see, for instance, the evolution of the rotational barrier around the terminal double bond); (ii) for a given polyene, the rotational barrier is lower for internal double bonds. The difference is important as may be seen for decapentene: 35 kcal/mol for the internal double bond, 37 kcal/mol for the intermediate one, and 45 kcal/mol for the external one. This result confirms some results indirectly obtained from ab initio studies of the lowest excited triplet minima in hexatriene.⁵³

The decrease of ΔR may appear to be very rapid, but one must remember that the largest visible wavelengths correspond to 35 kcal/mol, and that this energy is sufficient to induce the cis-trans isomerization around the internal double bond of retinal (a five- or six-conjugated double-bond compound); this 35-kcal/mol quantity necessarily represents an upper bound to the ground-state rotational barrier around the central bond of such a system, and this estimate is in good agreement with our result.

Another energetic remark would consist in comparing the π energies per electron for different molecules involving the same number of electrons. Cyclic molecules used to have larger π energies than the linear or branched ones; compare, for instance (in kcal/mol)

$n = 6$	benzene (217), fulvene (200), hexatriene (199), 2,3-dimethylene (167), butadiene (167)
$n = 10$	naphthalene (368), cyclodecapentene (349), azulene (343), decapentene (336)
$n = 8$	styrene (285), cyclooctatetraene (282), <i>p</i> - and <i>o</i> -xylylene (275), octatetraene (268), and metaxylylene (255)

The aromatic factor appears delightfully in this summary, despite the lack of specific aromatic six-body spin operators which stabilize these cycles.^{4,5} The instability of diradicals also appears strikingly.

These energies might be used to compare the absolute energies of *fully conjugated* isomers such as benzene, fulvene, and trimethylenecyclopropane, or azulene and naphthalene. The comparison will be worthless when important strain energies are implied, since we did not include them in our constant operator R , and strained cycles should not be included in such a comparison. (Notice however that the agreement with experimental geometries is almost the same for linear⁵⁵ and cyclic⁵⁶⁻⁵⁸ molecules.) The comparison would give the energy for fulvene 18 kcal/mol less stable than benzene, while experiment⁵⁹ gives 27 kcal/mol. A more relevant application would concern two C_8H_8 isomers (the *p*- and *o*-xylylenes), recently studied with the Dunning split valence basis set after an SCF STO-3G geometry optimization; our energy difference (19 kcal/mol in favor of the para quinoid compound) compares favorably with the best ab initio estimate⁵² (24 kcal/mol). The indirect experimental evidence from Hehre et al.⁵⁴ is

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(56) A. Langseth and B. P. Stoicheff, *Can. J. Phys.*, **34**, 350 (1956).

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(59) J. H. Day and C. Oestreich, *J. Org. Chem.*, **22**, 214 (1957).

consistent with an energy difference between 16 and 26 kcal/mol.

(F) Asymptotic Behavior of Rotational Barriers: Connection between Rotational Barriers and Solitons in Even Polyenes. In order to obtain some information about the properties of larger polyenes, extrapolations of the π energies have been attempted for odd and even liaison polyenes. The π energies are assumed to behave as

$$E_{\pi}(2n) = -2n \left(A - \frac{B'}{2n} - \frac{C'}{(2n)^2} \right) \quad (11)$$

$$E_{\pi}(2n+1) = -(2n+1) \left(A - \frac{B}{2n+1} - \frac{C}{(2n+1)^2} \right) \quad (12)$$

where the linear coefficient is necessarily identical, as previously discussed. The fitting over the largest calculated compounds leads to the following values (kcal/mol): $A = 34.4$, $B' = 8.0$, $C' = -2.8$, $B = 13.1$, and $C = 41.0$. From these expressions one may predict the asymptotic barriers around the *single bonds*, since for the most external single bond

$$\Delta \mathcal{R}_{4n,4n+1} = E_{\pi}(4n+2) - E_{\pi}(4n) - E_{\pi}(2)$$

which tends toward

$$\Delta \mathcal{R}_{4n,4n+1}^{(4n+2)} \rightarrow 2A - 62.5 \text{ kcal/mol} = 6.3 \text{ kcal/mol}$$

when n tends to infinity; in view of the rotation for butadiene (5.4 kcal/mol), this means an almost constant barrier.

For a rotation around an internal single bond, one should study the behavior of the rotation around the $2n$, $2n+1$ bond of a $4n$ polyene

$$\Delta \mathcal{R}_{2n,2n+1}^{(2n)} = E(4n) - 2E(2n)$$

which tends toward B' , i.e., 8.0 kcal/mol. This value is somewhat larger than the preceding one, as expected since the bond alternation is weaker in the central region of larger polyenes.

For the rotation around *double bonds*, similar extrapolations are possible (numerical values for $n < 18$ are given in Table II). The rotation around a *terminal* double bond should give

$$\Delta \mathcal{R}_{2n,2n}^{(2n)} = E_{\pi}(2n) - E_{\pi}(2n-1)$$

since the π energy of the methyl group is zero. This barrier tends toward

$$\Delta \mathcal{R}_{2n,2n}^{(2n)} \rightarrow A - B' + B = 39.5 \text{ kcal/mol}$$

The rotation around a central double bond in a $4n+2$ polyene is given by

$$\Delta \mathcal{R}_{2n+1,2n+2}^{(4n+2)} = E_{\pi}(4n+2) - 2E_{\pi}(2n+1)$$

which tends toward

$$\Delta \mathcal{R}_{2n+1,2n+2}^{(4n+2)} \rightarrow 2B - B' = 18.2 \text{ kcal/mol}$$

This rather low asymptotic value is again due to the weakening of the bond alternation in the central part of the molecule. Equations 11 and 12 enabled one to estimate the evolution of the rotational barrier $\Delta \mathcal{R}_{2p-1,2p}^{(4n+2)}$ as a function of both the size of the molecule and the position of the rotated bond in the molecule.

The large difference between the single- and double-bond rotational barriers in long polyenes confirms the bond alternation (or dimerization) phenomenon which has recently been experimentally proved in polyacetylene.⁶⁰ The proposed experimental alternation parameter ($u_0 = 0.03 \text{ \AA}$) is only approximate since it is a mean alternation over the chain, while our results (cf. decapentene in Figure 4) show that the alternation is stronger on external bonds than in the central part of the molecule. The experimental bond lengths for hexatriene⁵⁵ already exhibit this differential phenomenon.

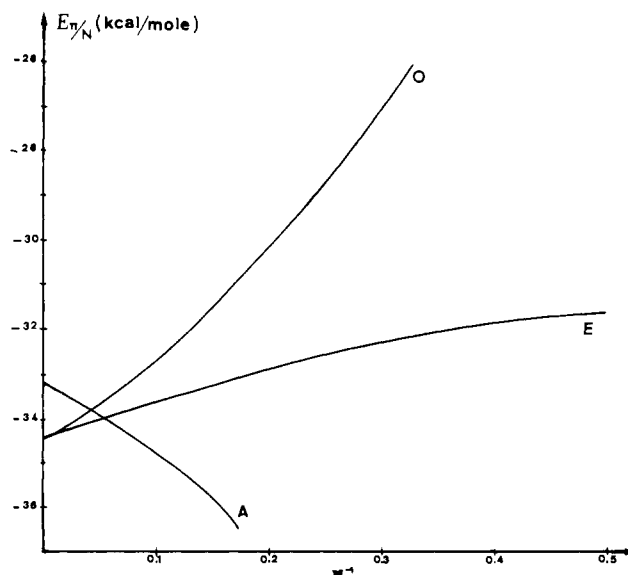
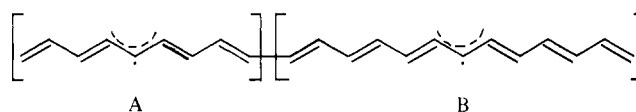
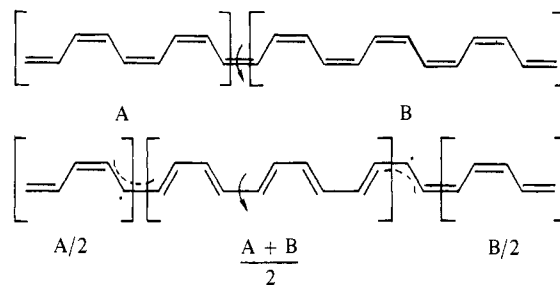


Figure 9. N dependence of the π energy per electron for odd (O), even (E) linear polyenes and cyclic annulenes (A).

One should notice that the transition state of the perpendicular system corresponds to two fully relaxed odd polyenes; the corresponding bond lengths



are those where a radical site occurs in the middle of both fragments A and B; all bond lengths keep their original alternation on the extreme parts of the molecule, while the bond lengths between the two radical sites are permuted; this reversion of the bond alternation concerns the internal half part of the molecule as schematically depicted below in the case of a cis chain. This



picture corresponds to the creation of a soliton pair, and introduces a transoid \rightarrow cisoid isomerization of the central part of the molecule. The energy to create a pair of solitons is obtained from the rotational barrier in a double bond by subtracting the rotational barrier around a single bond, in order to restore the planarity of the central cisoid part; the asymptotic value will be $18.2 - 8.0 = 10.2 \text{ kcal/mol}$.

As a further application of these extrapolations, one may try to predict the size of the cyclic even ring which will first present the tendency to bond alternation. The calculated energies reported in Figure 5 do not include some specific cyclic contributions which are important in small rings, but which should vanish for large n . The asymptotic value (33.2 kcal/mol) of the π energy per electron may be obtained from the exact solution for Heisenberg cyclic chains with equal bond lengths proposed by Hulten.⁶¹ This value is smaller (by 1.2 kcal/mol, i.e., 0.04 eV) than the asymptotic value for the dimerized chain, and one may expect, in view of Figure 9, that the dimerization should begin between 20 and 30 atoms in annulenes.

(60) C. R. Fincher, C. E. Chen, A. J. Heeger, A. G. McDiarmid, and J. B. Hastings, *Phys. Rev. Lett.*, **48**, 100 (1982).

(61) L. Hulten, *Ark. Mat. Astron. Fys.*, **26A**, 1 (1938).

Table III

		a_0	a_1	a_2	a_3	a_4	a_5
$\theta = 0$	g	0.827 913	-0.590 352	0.154 175	-0.014 702	-0.000 423	0.000 124
	R	19.437 242	-27.941 801	16.346 23	-4.877 829	0.743 522	-0.046 185
$\theta = 30^\circ$	g	4.143 833	-7.153 363	5.185 013	-1.908 907	0.352 069	-0.025 892
	R	10.706 896	-12.923 447	5.876 462	-1.196 986	0.092 805	0
$\theta = 45^\circ$	g	21.220 537	-37.938 315	27.272 021	-9.808 278	1.761 537	-0.126 297
	R	30.357 889	-48.645 617	31.716 776	-10.509 739	1.766 309	-0.120 009
$\theta = 60^\circ$	g	-76.982 553	140.797 163	-102.632 239	37.298 832	-5.760 164	0.488 887
	R	18.313 910	-26.870 589	15.944	-4.800 158	0.734 448	-0.045 561
$\theta = 90^\circ$	g	0.001 497	-0.103 834	0.146 597	-0.077 745	0.018 303	-0.001 612
	R	9.145 453	-10.991 265	4.933 581	-0.986 119	0.074 811	0

IV. Conclusion

A very simple Heisenberg Hamiltonian for conjugated hydrocarbons has been extracted from ab initio calculations of the ethylene molecule. In its present form the Hamiltonian is built from a scalar function and a two-body effective exchange operator (g) between bonded carbons. The scalar function is considered as a sum of bond increments, and both R_{ij} and g_{ij} are functions of the interatomic distance r_{ij} and the torsional angle θ_{ij} between the bonded atoms i and j .

Most of the calculations reported above concerned only the ground-state planar conformations, for which the agreement with experiment was extremely good (the standard deviation from experiment being 0.01 Å), despite the very small computational effort required for this type of treatment. The study of rotational barriers is as easy as that of planar conformations since hyperconjugative effects are correctly taken into account in the basic information; it may be achieved without any assumption about a regular progression of the C-C bond-length changes from the planar to the twisted conformation, improving therefore the determination of the minimum energy paths along the cis-trans isomerization process, and it avoids the MO dilemma for rotational barrier studies (closed-shell/open-shell description of the planar/perpendicular conformations).

The method may be compared to semiempirical studies which add a σ compressibility function to a π -energy calculation. The π -energy calculation may rest on a Hückel-type model as in Su et al.⁴⁴ soliton study, or on a PPP or Hubbard CI calculation, as in the work of Lasaga et al.²⁰ The effective valence bond model includes most of the π correlation effects, as previously shown,^{4,5} since it reproduces the PPP full CI solutions; in its present version it also includes $\sigma\pi$ correlation effects. Since it takes into account hyperconjugative effects, it may treat nonplanar conformations, for which the $\sigma\pi$ additivity scheme used to break down. Moreover, its diagonalization step is much cheaper than the full π CI diagonalization.

The method might be improved in three directions: (i) by including three- (rather small) and four-body operators. (the four-body operators are only important in four-membered rings and might be extracted easily from a few calculations on cyclobutadiene); (ii) by considering other geometric parameters (valence angles) and their influence on R (and to a lesser extent on g) and by adding to R a few long-distance repulsion terms necessary to take into account steric effects; (iii) by considering substitution effects by methyl groups (or even heteroatoms) which might be obtained from calculations on propene (or $>C = X$ systems).

The resulting predictions for ground-state conformations are in good agreement with experiment, but most of the quantum chemical methods succeed in this type of problem. It also succeeds in predicting isomerization energies between unstrained fully conjugated isomers. The method is more interesting when applied to nonstandard problems, such as open-shell systems, radicals, or diradicals, for which experiment is lacking, owing to their transient character, and where standard MO methods are not easily defined. The method might be applied to the soliton problem,⁴⁴ giving information including correlation effects. The present results suggest a stronger localization of the soliton radical deformation than uncorrelated models which predict that it concerns about 14 bonds. The energy required to move the soliton from its minimum energy conformation on the center of the molecule has

Table IV. Convergence of the Bond Lengths l_{ij} (in Å) and of the Wave Function (Probability to Find a Singlet Arrangement between Atoms i and j , \mathcal{P}_{ij}^S) along the Geometry Optimization

iteration	0	1	2	3	4
l_{1-2}	2.588	2.596	2.607	2.611	2.612
\mathcal{P}_{1-2}^S	0.839	0.807	0.796	0.792	0.790
l_{2-3}	2.741	2.686	2.673	2.668	2.667
\mathcal{P}_{2-3}^S	0.577	0.614	0.628	0.632	0.634
l_{1-9}	2.741	2.691	2.679	2.676	2.675
\mathcal{P}_{1-9}^S	0.563	0.596	0.606	0.610	0.611
l_{9-10}	2.588	2.637	2.654	2.660	2.662
\mathcal{P}_{9-10}^S	0.720	0.669	0.652	0.647	0.645

been calculated for $n = 9$ and $n = 11$ linear chains, by translating the deformation along two C-C bonds (cf. Figure 6). The loss of energy for such a displacement is a very weak (1 kcal/mol for $n = 9$, 1.2 kcal/mol for $n = 11$), showing the extreme mobility of the soliton. The method might be applied to larger compounds; one might determine the surface of the ground-state energy as a function of the C-C bond lengths and apply the trajectory methods, which have been so successful in chemical reactivity problems, in order to study the diffusion of the soliton created on one side of the system.

The present paper presents only a few examples of excited-state studies (for instance, trimethylenemethane singlet, subject to a Jahn-Teller effect), which appeared to compare perfectly with ab initio results.⁴⁶ The main interest of the method may concern neutral excited-state potential surfaces. For excited states standard MO techniques are not available since there is no reliable single determinant approximation to start from (because of near-degeneracy effects) and the required CI's are larger than for the ground state. Moreover, the excited states of linear and branched polyenes tend to twist in the excited states, preventing simple $\sigma-\pi$ separation schemes. The following paper is devoted to the neutral excited-state properties.

Appendix I

The coefficients of polynomial expansion

$$g = \sum_{i=1}^5 a_i - x^i, R = \sum_{i=1}^5 a_i' x^i$$

are given in Table III. Energies are in atomic units, distances in bohrs.

Appendix II

Table IV illustrates the convergence properties of the geometry optimization algorithm, in the case of naphthalene (with the standard numbering of atoms) ground state.

Registry No. C₂H₄, 74-85-1; C₃H₅, 1981-80-2; C₄H₆, 106-99-0; C₆H₇, 3808-35-3; C₆H₈, 2235-12-3; C₇H₉, 15671-45-1; C₈H₁₀, 1482-91-3; C₉H₁₁, 15671-46-2; C₁₀H₁₂, 2423-91-8; C₁₁H₁₃, 15671-47-3; C₁₂H₁₄, 2423-92-9; C₁₄H₁₆, 2423-93-0; C₁₆H₁₈, 2588-89-8; C₁₈H₂₀, 3227-86-9; C₂₀H₂₂, 2423-94-1; 2,4-cyclopentadien-1-yl, 2143-53-5; 2-methylene-1,3-propanediyl, 13001-05-3; 2-methylene-3-butenyl, 31922-49-3; 2,3-dimethylene-1,4-butanediyl, 16893-57-5; tris(methylene)cyclopropane, 3227-90-5; fulvene, 497-20-1; azulene, 275-51-4; naphthalene, 91-20-3; toluene, 108-88-3; styrene, 100-42-5; 5,6-bis(methylene)-1,3-cyclohexadiene, 32796-95-5; 3,6-bis(methylene)-1,4-cyclohexadiene, 502-86-3; 1,3-phenylenebis(methyl), 32714-83-3.